



PATENT SPECIFICATION

665,474

Date of Application and filing Complete Specification Dec. 31, 1948.

No. 33633/48.

Complete Specification Published Jan. 23, 1952.

Index at acceptance:—Classes 2(iii), C2a19, I(1:2); 2(iv), F; and 2(v), R2c6, R2m(1:2), R3c6, R3d(4:5:10:11), R3m(2:3:4), R6(c6:m), R7(c6:m), R19(c6:m), R22(c6:m), RP11d(2x:4:7), RP11plel.

COMPLETE SPECIFICATION

Cation Modified Clay

I, STANLEY GUSTAV DEHN, M.A., a British Subject, Chartered Patent Agent, of Kingsway House, 103, Kingsway, London, W.C.2, do hereby declare the nature of this invention (a communication to me from National Lead Company, a corporation duly organized under the laws of the State of New Jersey, United States of America,) of 111, Broadway, New York, State of New York, United States of America,) and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to modified clays which are the reaction products of organic base clay compounds and other reactable organic compounds.

As found in nature, clays exhibiting base-exchange properties exist as salts of the clay acid with inorganic bases such as the alkalis and alkaline earths. Certain colloidal clays are known to process substantial base-exchange capacities. Examples of such clays are monmorillonites, such as sodium, potassium and lithium bentonites; magnesium bentonite sometimes called hectorite and saponite, and a group of compounds such as nontronite, illite, attapulgite, fullers earth and synthetic inorganic materials, such as permutites. These clays have base exchange capacities of from 40 to 120 milli-equivalents per gram of clay. Some of these clays, such as the bentonites when placed in water, will swell to many times their volumes. If the particles of such clays, chemically reacted with certain organic compounds which may be generally designated as "onium" compounds, the metal clay cation will base-exchange with the radical of the organic onium compound to form an organic base clay. This reaction so modifies the surfaces of the clay that it may be made further reactable to other organic compounds so as to become useful in organic systems such as plastics,

resins, rubbers, or paints.

An onium compound has been defined in Hackh's Chemical Dictionary, Second Edition, as a group of organic compounds of the type RXH_y which are isologs of ammonium and contain the element X in its highest positive valency, viz: where X is pentavalent as in ammonium, phosphonium, arsonium and stibonium; where X is tetravalent as in oxonium, sulfonium, selenonium and stannonium compounds; and where X is trivalent, as in iodonium compounds; these compounds may be considered addition compounds.

R is in the present invention an organic radical, for example, a hydrocarbon chain, a fatty acid radical, an aromatic group and so on.

According to the present invention there is provided a process for the treatment of clays having originally substantial base-exchange capacity, characterized by the feature that such clay is reacted with an onium compound of the character described by substitution of the clay cation with the organic onium cation and further reacted with an organic compound whose radical has an affinity to the organic portion of the onium radical by substitution for a hydrogen thereof, which reaction so modifies the surfaces of the clay that it may be made further reactable to other organic compounds so as to become useful in organic systems such as plastics, rubbers or paints.

In accordance with this invention a clay of the character described is reacted with an onium compound of the character described and subsequently with other organic compounds reactable with the organic portion of the onium compound, in condensation, polymerization, esterification, or substitution reactions. The latter reactable organic compounds comprise agents which may form resins with the organic portion of the onium compound such as aldehydes, ketones, polycarboxy-

[Price

lic acids and anhydrides such as adipic acid, phthalic anhydride and maleic anhydride, fatty acids, dyes and dye intermediates, synthetic resins, natural and synthetic rubbers, and other organic compounds which are capable of self-polymerization reactions.

In accordance with this invention, a clay originally exhibiting substantial base exchange capacity, is reacted with an onium compound of the character described, by substitution of the clay cation for the organic cation and further reacted with an organic compound capable of reacting with the organic portion of the onium radical by substitution for a hydrogen thereof. Where the onium compound is polybasic, the substitution of the clay cation is with one of the basic onium groups, and the radical of the organic compound may have an affinity to another of the basic onium groups, or to the organic portion of the poly-onium compound. The reaction is such that there is no disrupting of the linkage of the onium compound with the clay anion.

The products of this invention which are the reaction products of an onium clay compound and a reactable organic compound as defined above, comprise thermoplastic and thermosetting plastics, colored pigments, reinforced rubbers, alkyd resins and resin intermediates, as well as onium clay complexes with fatty acids.

The process generally comprises adding the reactable organic compound to the converted onium clay. The converted onium clay generally may be prepared as described in the illustrative examples of this invention. In general the converted onium clays used are clays which have been base-exchanged with organic bases in a ratio of substantial saturation of the base-exchange capacity of the clay, viz: for Wyoming bentonite, 100 milliequivalents per 100 grams of clay; but in accordance with this invention, it is not necessary that the products produced represent complete replacement of the inorganic cation by the onium base. Due to its small average particle size and high base-exchange capacity, bentonite is well adapted for use in the practice of this invention. The invention, however, is not limited to this clay but any of the other clays previously enumerated may be used as a starting material and primarily reacted with any of the onium compounds enumerated and secondarily reacted with the reactable organic compounds enumerated, all as illustrated by the examples hereinafter given.

The clays may be modified in one of several directions to give properties which

are markedly different from those commonly exhibited by clays. For instance, the onium clays further reacted with certain organic compounds capable of forming with said onium clay compounds having the nature of synthetic plastics result in reaction products which are thermoplastics and thermosetting materials in which a higher loading of clay is possible and in which the clay contributes valuable properties such as heat resistance. The onium clays may be further reacted to become valuable colored pigments in which the organic dye is stabilized against fading as well as insolubilized against "bleeding" in oil vehicles or plasticized resins, for instance. The onium base clays may also be further reacted in plastic and rubber systems where they offer superior reinforcement to that obtained by the use of organic clays which are not as compatible with the organic systems in question.

Various examples of modified clays embodying this invention will now be described.

EXAMPLE 1.

26.3 g. of octadecadienylamine were dissolved in 300 ml. of hot water and 10 g of 37% hydrochloric acid. After the amine had completely dissolved, a water slurry of 100 g of Wyoming bentonite was added thereto with vigorous agitation. The flocculant precipitate of octadecadienylammonium bentonite was suction filtered, washed and dried and the product was then ground with 1 g of benzoyl peroxide. The powder obtained may be molded and when molded at 150 C in 2 tons per square inch pressure, polymerization takes place and an integral product having the nature of a synthetic plastic product is achieved.

EXAMPLE 2.

As an example of the preparation of a thermoplastic product, 124 g of dry bentonite were stirred into 1800 ml of water to which had been added 93 g (1 mol) of aniline and 100 g (1 mol) of 37% hydrochloric acid. After thorough dispersion of the bentonite throughout the phenyl ammonium chloride solution to form the aniline bentonite in suspension, 120 g of 40% formalin (1.6 mol formaldehyde) were added. After 10 minutes during which time the exothermic reaction of aldehyde with amine has been progressing, the acid catalyst was neutralized and the reaction consequently stopped by addition of about 800 ml of 5% NaOH solution, or sufficient to bring the pH of the system to about 7. The flocculent yellow precipitate was filtered, washed thoroughly to remove electrolytes, dried and ground.

When mixed with 0.5—1.0% of zinc stearate mold lubricant and molded at 165° C. to 175° C. under a pressure of 2 to 3 tons per square inch, the powder is converted to a hard, tough, red-brown, thermosetting opaque solid of low water-absorbing capacity.

EXAMPLE 3.

As an example of the preparation of a thermosetting plastic product, 100 g of bentonite were dispersed in 2 liters of water, and 14.6 g (0.1 mol per 100 g bentonite) of triethylene tetramine stirred into the dispersion. The pH was brought to 6.6 by the addition of approximately 24 g (0.4 mol) of acetic acid, thus converting the amine to the acetate to insure thorough reaction with the bentonite and establishing a desirable pH for the ureaformaldehyde resin into which the mixture was incorporated. At this stage, three fourths of the amine groups remained available for condensation. The flocculent, triethylene tetrammonium bentonite precipitate was filtered, washed and milled with 107 g of 42% aqueous solution of dimethylol urea and 0.5 g of zinc stearate on hot differential rolls until dry and well sheeted. The sheet when cooled ground and molded at 165° C. under 2 to 3 tons per square inch, producing a hard tough, olive-green thermoset solid of good mechanical strength.

EXAMPLE 4.

An example of the preparation of a pigment is as follows: 18.4 g of benzidine were dissolved in 300 ml of distilled water and 17.7 ml of concentrated HCl. This solution was added to 4200 ml of 2.39% bentonite slurry previously cooled to 0°—5° C. After thorough stirring, 26.5 ml of concentrated HCl were added. Flocculation of the benzidine bentonite occurred but in no way interfered with subsequent tetrazotization. 13.8 g of NaNO₂ dissolved in 800 ml of distilled water were then added drop by drop to the rapidly stirring cold slurry. To insure complete reaction, stirring was continued for 2 hours after the nitrite addition was completed.

28.6 g of alphanaphthylamine were dissolved in a solution of 300 ml of distilled water and 17.6 ml of concentrated HCl. The resulting solution was added to the above cold stirring tetrazonium chloride slurry, and coupling occurred, and the deep red-brown dye flocculated the azotized bentonite compound. The resulting pigment suction filtered easily. The filter cake was dried in a suction desiccator at 110° C. in a current of CO₂. The product was a deep reddish brown and

ground quite easily. It is useful as a pigment in paints, or enamels.

EXAMPLE 5.

As a further example of the preparation of a pigment, 1.26 g of melamine were dissolved in 100 ml of hot water and 5 ml of concentrated hydrochloric acid, 37% strength. The hot solution was added to 415 g of a 2.41% bentonite slurry, forming melamine bentonite. 4.36 g of Ponceau red were dissolved in 100 ml of hot water. The hot dye solution was then added to the boiling amine bentonite amine bentonite slurry and stirred. A flocculant precipitate formed readily and was suction filtered. The filter cake after being dried and ground was a soft powder useful for paints, enamels, etc.

EXAMPLE 6.

The procedure of Example 5 was followed except that an equivalent hot slurry of fuller's earth (attapulgit) from Quincy, Florida was used in place of bentonite. A similar product was obtained.

EXAMPLE 7.

The procedure of Example 5 was followed except that an equivalent hot slurry of a synthetic zeolite was used in place of bentonite. A similar product was obtained.

EXAMPLE 8.

The procedure of Example 5 was followed except that an equivalent hot slurry of a magnesium bentonite from Hector, California was used in place of bentonite. A similar product was obtained.

EXAMPLE 9.

The procedure of Example 5 was followed except that an equivalent hot slurry of nontronite from Cameron, Arizona was used in place of bentonite. A similar product was obtained.

EXAMPLE 10.

As an example of the preparation of a bentonite alkyd resin, 19.8 g of 37% hydrochloric acid were dissolved in 1600 ml of water. 15 g of glycerine were added thereto and then 238.8 g of steam jet milled Wyoming bentonite were added while stirring for 30 minutes. The flocculant precipitate of glycine bentonite which formed was filtered, washed, dried and ground. 150 g of this product, together with 90 g of glycerine, were placed in a three-neck reaction flask and 200 g of toluol were added and the mass heated while stirring to 180 C. This temperature was held for 3 hours after which time 148 g of phthalic anhydride were slowly added to the mass. After an additional stirring of about 1 hour, the resinous mass became quite viscous and

stirring was discontinued. After being cooled, the bentonite alkyd resin formed was capable of being employed as a hard resinous plastic.

EXAMPLE 11.

- 600 g of Wyoming bentonite were allowed to stand in 18 liters of water to settle out the non-clay impurities. 9.9 g of 37% hydrochloric acid were added to 14.92 g of triethanolamine and the salt formed was then dissolved in 3 liters of hot water, which solution was added to 2924 ml of the grit-free bentonite slurry, above mentioned. Flocculation of the bentonite occurred immediately and the precipitate was filtered, washed, dried and ground 362.5 g of phthalic anhydride were then added to 65 g of the triethanolamine bentonite and heated in 500 g of toluol. After the temperature had been held at 200 C. for 2 hours, 302.5 g of soybean fatty acids, 7.5 g of fumaric acid and 210 g of glycerine were added thereto and the mass held at 200 C. for an additional 6 hours. After cooling, a viscous resinous solution was obtained which when applied as a film forming coating material, was found to air-dry to a hard coating in about 6 hours.

EXAMPLE 12.

- 1149.2 g of triethanol amine bentonite, prepared as described in Example 11, and 853.4 g of stearic acid were heated together to 280° C. and held at this temperature for 5 hours. The triethanol amine bentonitetriscarate which formed was found to be useful as a gelling agent in organic liquids.

EXAMPLE 13.

- 1149.2 g of triethanol amine bentonite, prepared as described in Example 11, and 432.92 g of adipic acid were heated together to 250° C. and held at this temperature for 5 hours. The triethanol amine bentonitetriadipate product formed was found to be useful as a condensation resin intermediate which when combined with drying oil fatty acids and glycerine in the presence of phthalic anhydride, formed viscous resin solutions which may be applied as a film forming coating.

EXAMPLE 14.

- 1149.2 g of triethanol amine bentonite, prepared as described in Example 12, and 281.47 g of stearic acid were heated to 280° C. and held at this temperature for 5 hours. The product which formed, triethanol amine bentonitemonostearate, is useful as a condensation resin intermediate and when combined with drying oil fatty acids and glycerine in the presence of phthalic anhydride, forming viscous resin solutions which may be applied as film forming coatings.

EXAMPLE 15.

10.3 g of diethylene triamine was dissolved in 100 ml of water and 30 g of 37% hydrochloric acid. After the solution was complete, a water slurry of 271 g of illite was added with vigorous agitation. The flocculant precipitate was filtered, washed, dried and ground. This powder was then thoroughly mixed with 9.8 g of maleic anhydride. Upon molding at 150° C., amidification of the maleic anhydride with the two remaining amine groups and condensation took place and the entire mass became an integral unit.

EXAMPLE 16.

The process of Example 11 is carried out, except that instead of 14.9 grams of triethanolamine, the equivalent weight of triethanolethyl arsonium iodine was used, the 9.9 grams of hydrochloric acid specified in Example 11 being omitted. The rest of the process is carried out as set forth in Example 11.

EXAMPLE 17.

The process of Example 16 is carried out except in place of triethanolethyl arsonium iodine, an equivalent quantity of triethanolethyl stibonium iodine is used.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that what I claim is:—

1. A process for the treatment of clays having originally substantial base-exchange capacity, characterized by the feature that such clay is reacted with an onium compound of the character described by substitution of the clay cation with the organic onium cation and further reacted with an organic compound whose radical has an affinity to the organic portion of the onium radical by substitution for a hydrogen thereof, which reaction so modifies the surfaces of the clay that it may be made further reactable to other organic compounds so as to become useful in organic systems such as plastics, resins, rubbers or paints.

2. The process as claimed in claim 1, characterized by the feature that one of the basic onium groups of a polybasic onium compound is substituted for the clay cation while the organic compound has an affinity to another of the basic onium groups.

3. The process as claimed in claims 1 or 2, characterized by the feature that the substitution is without disruption of the linkage of the onium compound with the clay anion.

4. The process as claimed in claims 1, 2 or 3, characterized by the feature that

the clay starting material is a bentonite.

5. A modified clay base product which has been produced by replacing the natural inorganic cation thereof with an organic radical of an onium compound and by further replacing a hydrogen of the latter with a radical of an organic compound which has an affinity to the onium compound.

10 6. A modified clay base produced as claimed in claim 5, characterized by the feature that a polybasic onium compound has basic groups, one of which is the sub-

stituted cation and the other of which is substituted with a radical of the organic 15 compound.

7. A process for producing a cation modified clay substantially as described.

8. A modified clay base substantially as described.

Dated this 31st day of December, 1948.

For the Applicant:

FRANK B. DEHN & CO.,
Chartered Patent Agents,
Kingsway House, 103, Kingsway,
London, W.C.2.

20

Leamington Spa: Printed for His Majesty's Stationery Office, by the Courier Press.—1952.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which
copies, price 2s. per copy; by post 2s. 1d. may be obtained.

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.